

## Supporting Information

### **Application of multifunctional magnetic mesoporous material for seafood samples clean-up prior to the determination of highly chlorinated polychlorinated biphenyls**

Haibo Liu <sup>a, #</sup>, Jiabin Zhang <sup>a, #</sup>, Ning Gan <sup>a, \*</sup>, Yinji Chen <sup>b, \*\*</sup>, Jie Huang <sup>c</sup>, Yuting Cao

<sup>a</sup>, Tianhua Li <sup>a</sup>, Hangzhen Lan <sup>c</sup>

a. Faculty of Materials Science and Chemical Engineering, Ningbo University,

Ningbo, 315211, China

b. Department of Food Science and Engineering/Collaborative Innovation Center for

Modern Grain Circulation and Safety, Nanjing University of Finance and Economics,

Nanjing, 210046, China

c. Faculty of Marine Science, Ningbo University, Ningbo, 315211, China

#. They have made the same contribution to this article

\*.Corresponding author. Tel.: +86 574 87608347; fax: +86 574 87608347.

E-mail addresses: [ganning@nbu.edu.cn](mailto:ganning@nbu.edu.cn), [chenyinji@gmail.com](mailto:chenyinji@gmail.com).

**Table S1** The qualitative ion, quantitative ion, retention time of PCBs and OCPs

The peak number	PCB and OCP	retention time t (min)	quantitative ion (m/z)	qualitative ion (m/z)
1	PCB 52	10.730	292	290, 220
2	PCB 101	12.411	326	256, 324
5	PCB 153	14.502	360	290, 362
7	PCB 138	15.306	360	290, 362
8	PCB 180	17.427	396	324, 394
3	p,p'-DDE	13.045	246	248, 318
4	p,p'-DDD	14.100	235	237, 251
6	p,p'-DDT	15.140	235	165, 199

**Table S2** Method quality parameters obtained in real shellfish matrix

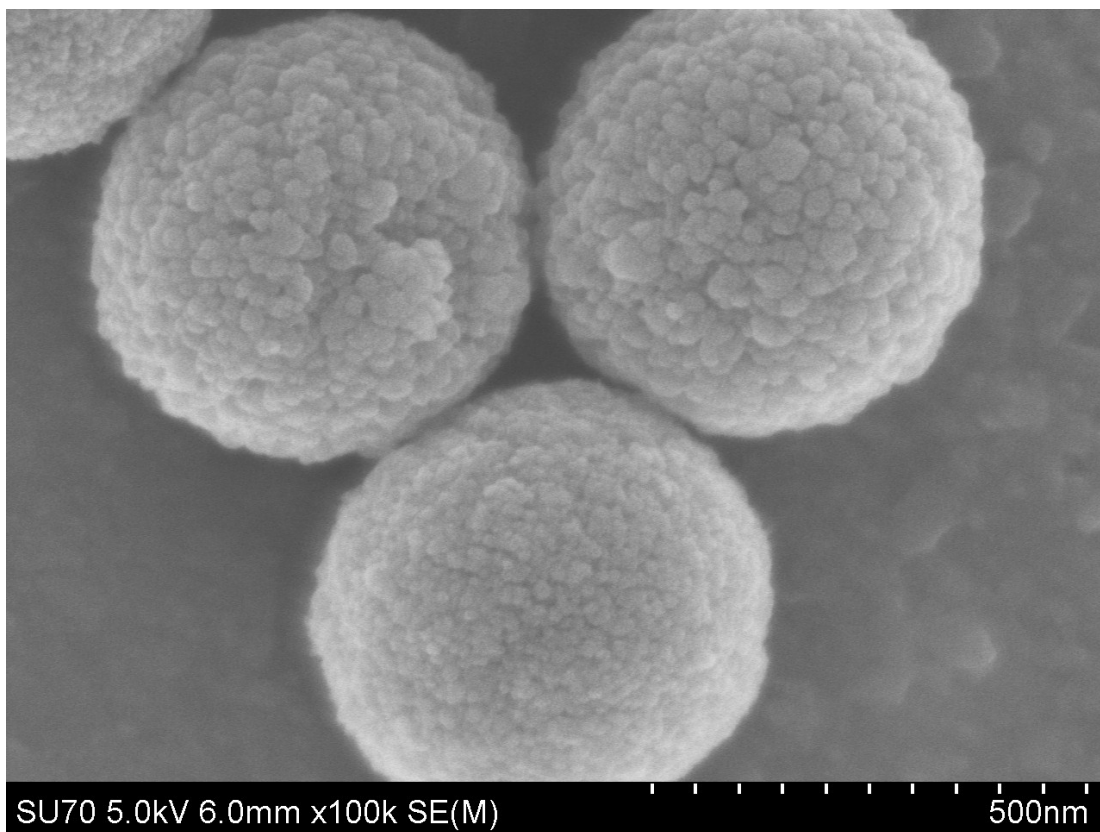
Analytes	Calibration equations	Linear range ( $\mu\text{g}\cdot\text{L}^{-1}$ )	correlation coefficients(r)	LOD ( $\text{ng}\cdot\text{g}^{-1}$ )	LOQ ( $\text{ng}\cdot\text{g}^{-1}$ )
PCB52	$y=279.96x+85.40$	0.1-200	0.9991	0.025	0.07
PCB101	$y=254.02x+78.95$	0.1-200	0.9998	0.034	0.11
PCB138	$y=250.52x+92.69$	0.2-200	0.9989	0.038	0.12
PCB153	$y=284.77x+75.67$	0.2-200	0.9993	0.057	0.17
PCB180	$y=296.72x-47.45$	0.3-200	0.9987	0.071	0.22

**Table S3** Recoveries for each analyte at fortification levels in fish and shellfish matrix: 0.5 and10 ng·g<sup>-1</sup>

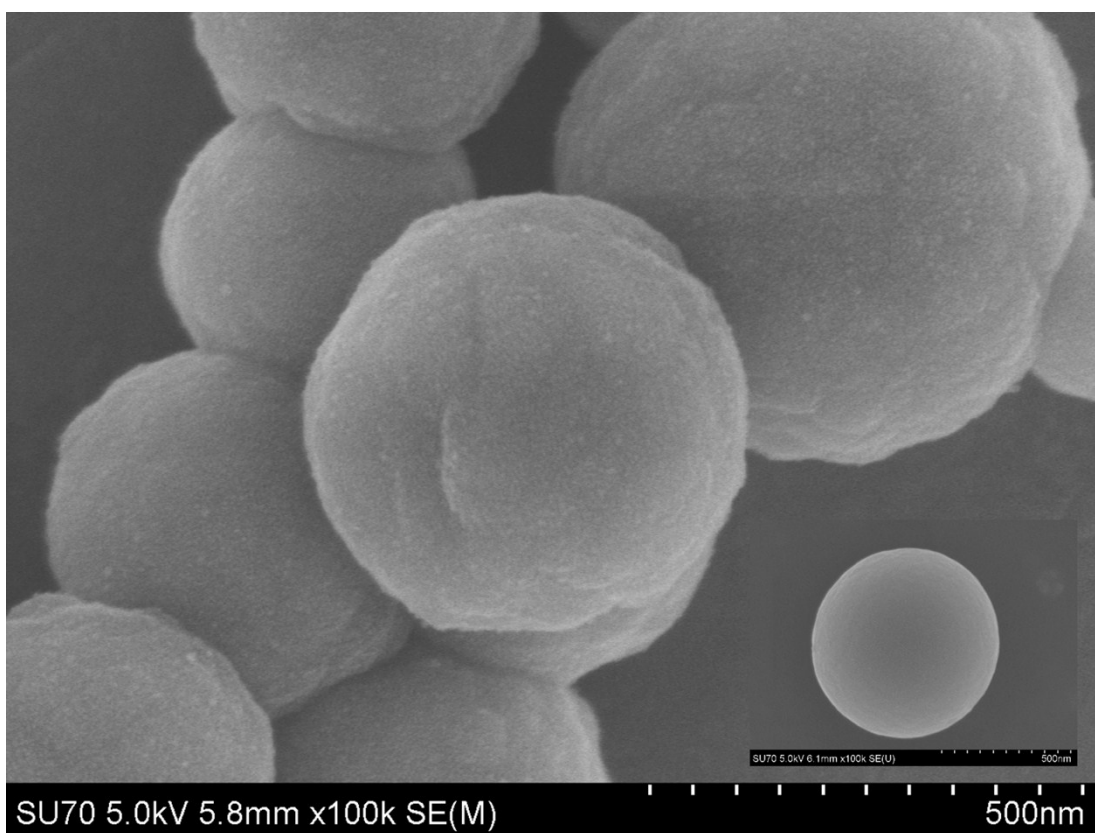
PCBs	Added (ng·g <sup>-1</sup> )	Recovery(%)±RSD						
		yellow croaker	silver pomfret	hairtail	shad fish	oyster	mussels	scallop
PCB52	0.5	92±2	93±3	88±5	89±3	84±9	100±5	94±5
	10	89±3	97±5	94±2	88±4	90±5	102±11	96±7
PCB101	0.5	95±2	93±4	96±6	94±4	89±4	93±6	89±2
	10	97±6	103±4	97±9	93±6	98±3	94±2	87±3
PCB138	0.5	102±9	105±5	96±2	92±2	100±3	89±8	95±4
	10	96±8	87±6	94±5	93±2	102±8	93±2	92±6
PCB153	0.5	101±6	84±7	93±5	95±1	85±6	95±7	91±2
	10	87±2	92±8	97±8	83±6	86±2	97±3	86±7
PCB180	0.5	90±9	96±3	103±3	93±6	96±5	105±5	82±4
	10	85±7	99±2	94±2	95±9	98±3	97±4	83±5

**Table S4** PCB concentrations ( $\text{ng}\cdot\text{g}^{-1}$ ) found in different real sample (n=3)

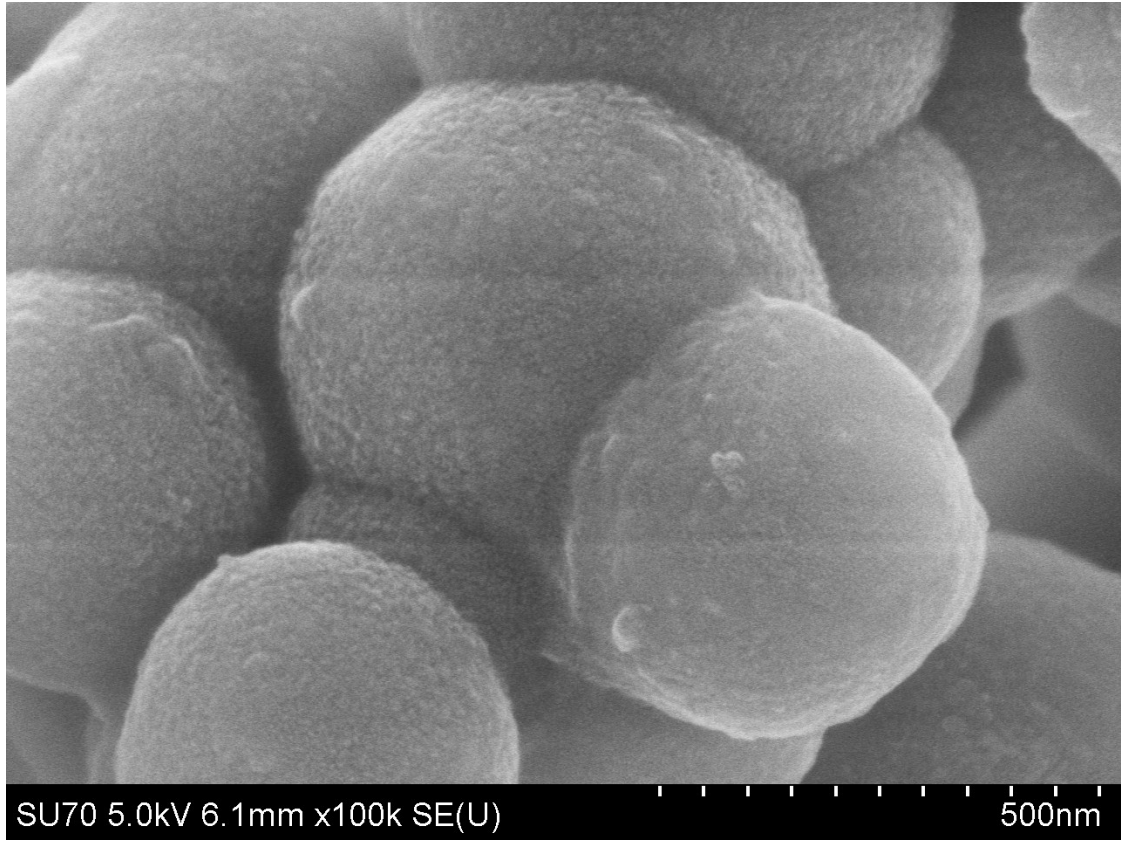
Sample	PCB52(%RSD)	PCB101(%RSD)	PCB153(%RSD)	PCB138(%RSD)	PCB180(%RSD)
yellow croaker	1.43(3.4)	ND	2.05(2.2)	ND	ND
silver pomfret	1.25(5.3)	6.69(7.2)	0.46(3.1)	ND	ND
hairtail	ND	ND	3.28(2.1)	ND	ND
shad fish	ND	ND	ND	ND	ND
oyster	0.75(1.9)	ND	ND	0.45(4.6)	ND
mussels	ND	ND	ND	1.73(3.2)	ND
scallop	ND	ND	ND	ND	ND



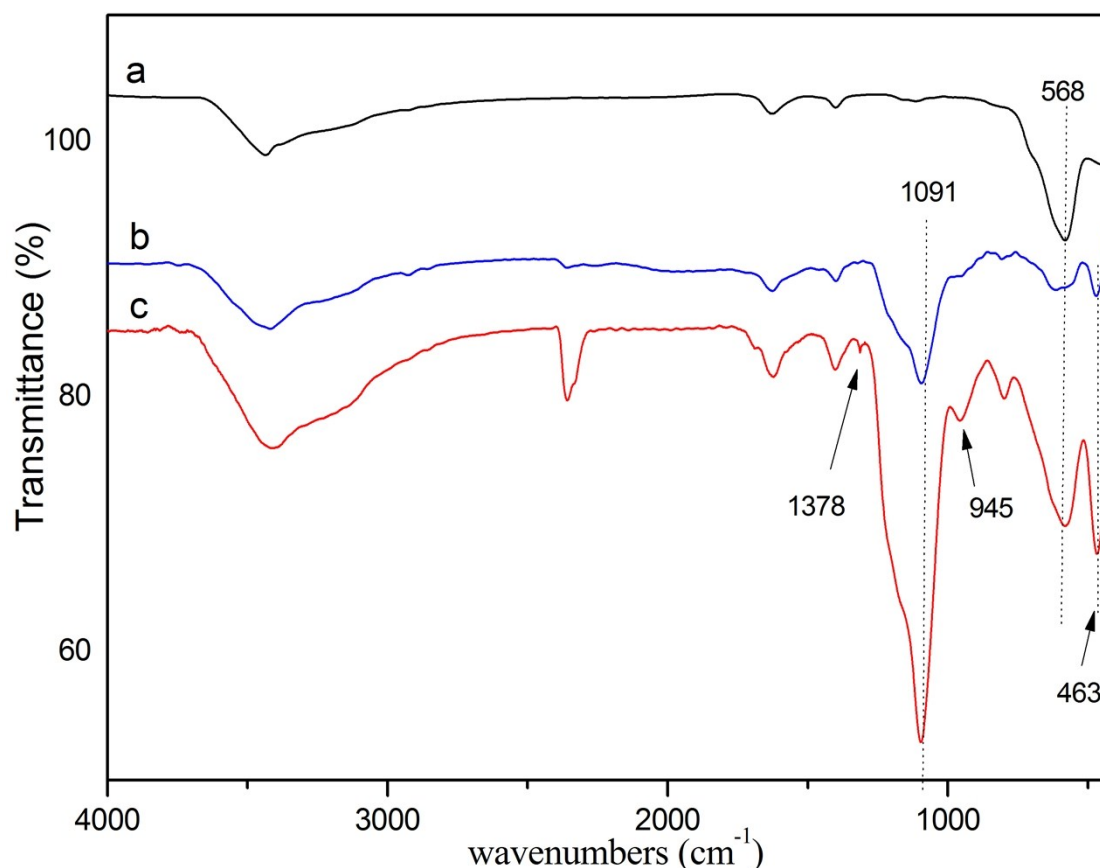
**Fig. S1a.** SEM image of  $\text{Fe}_3\text{O}_4$ .



**Fig. S1b.** SEM image of  $\text{Fe}_3\text{O}_4@m\text{SiO}_2$ , inset:  $\text{Fe}_3\text{O}_4@m\text{SiO}_2$  (the lower right corner).



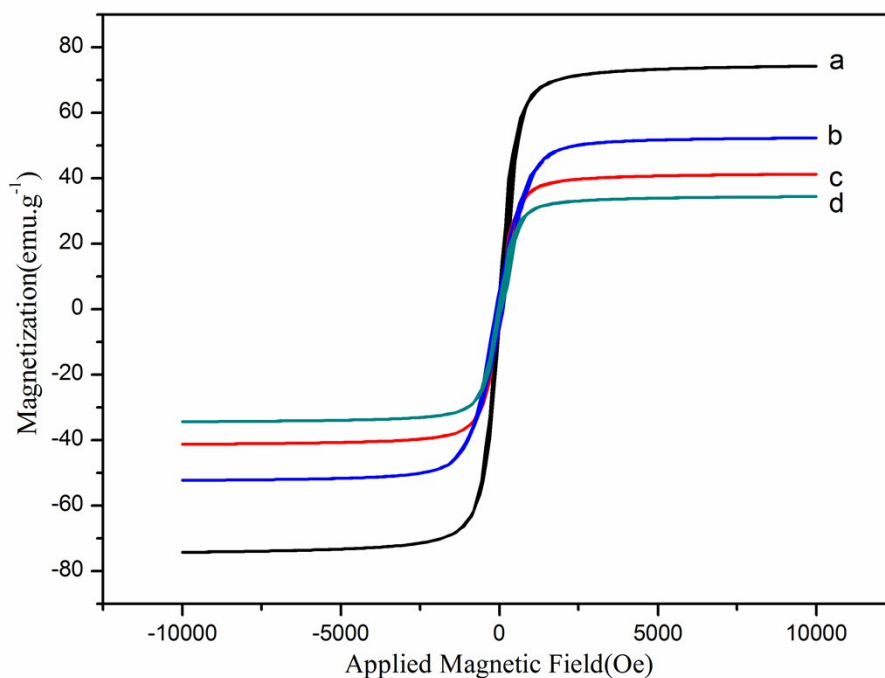
**Fig. S1c.** SEM image of  $\text{Fe}_3\text{O}_4@m\text{SiO}_2\text{-NH}_2\text{-CMCD}$ .



**Fig. S2.** FTIR spectra of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , (c)  $\text{Fe}_3\text{O}_4@m\text{SiO}_2\text{-NH}_2\text{-CMCD}$ .

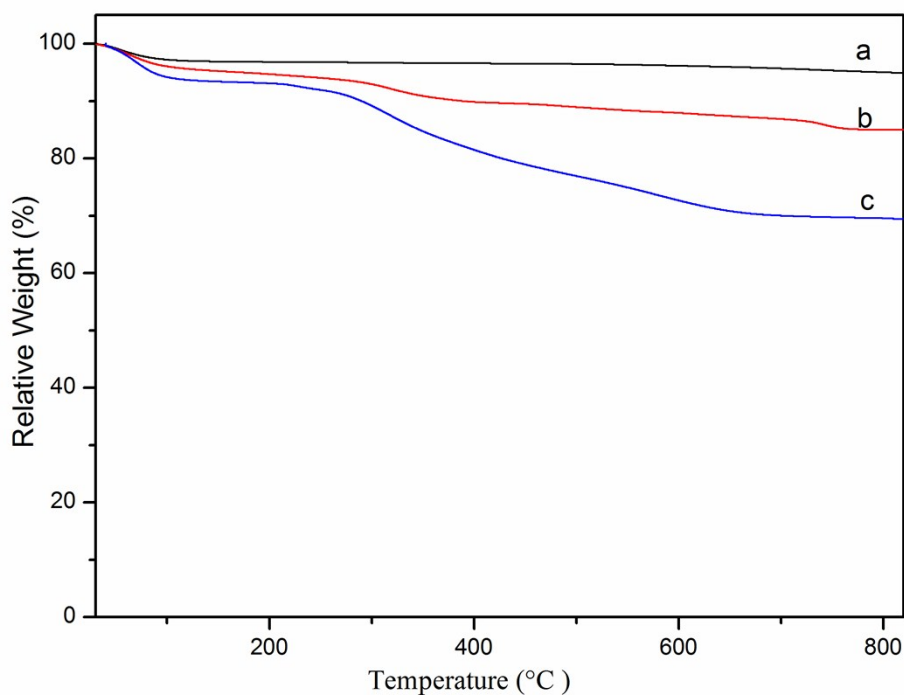
It is shown that the characteristic adsorption band of Fe-O is at  $586\text{ cm}^{-1}$  (Fig. S2a). The existence of the characteristic Si-O-Si stretching is shown at  $1091$  and  $463\text{ cm}^{-1}$  (Fig. S2b). Thus, it proves that the silica shell is linked to the surface of the magnetic  $\text{Fe}_3\text{O}_4$ . The main characteristic peaks of CM- $\beta$ -CD in the region of  $900\text{--}1200\text{ cm}^{-1}$  might have been overlapped by the strong peak due to silica coating. The peak at  $945\text{ cm}^{-1}$  is due to the R-1,4-bond skeleton vibration of  $\beta$ -CD (Fig. S2c). The absorption bands at  $1378\text{ cm}^{-1}$  is in correspond to symmetric stretching vibration of C-O groups in  $\beta$ -CD, which prove successful grafting of CM- $\beta$ -CD on silica coated magnetic nanoparticles.





**Fig. S3** VSM curves of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, (c) Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>, and (d) Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD

Fig. S3 shows the magnetization curves of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD at room temperature. The maximum saturation magnetization of Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD was 31.2 emu·g<sup>-1</sup>, which was lower than that of Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub> (41.2 emu·g<sup>-1</sup>). This might be attributed to the non-magnetic surface of mSiO<sub>2</sub>, cross-linking agents and CM-β-CD. Thus, the magnetic adsorbents carrying the interference matrix can be easily isolated from the clean-up procedures using an external magnet.



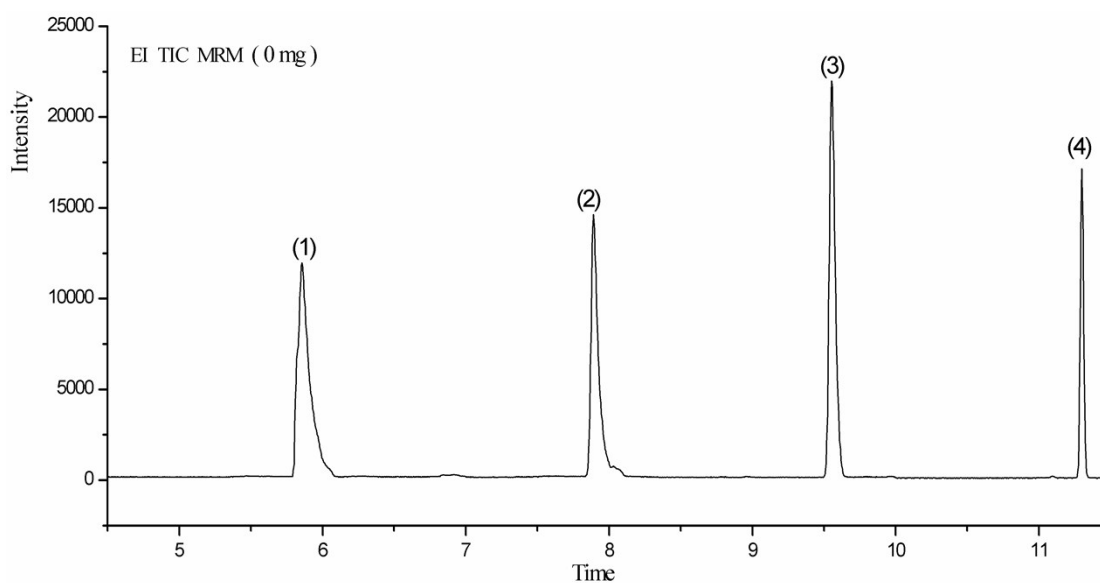
**Fig. S4** TGA curves of (a)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , (b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-CMCD}$  and (c)  $\text{Fe}_3\text{O}_4@m\text{SiO}_2\text{-NH}_2\text{-CMCD}$

Fig. S4 shows the TGA curves of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-CMCD}$  (not mesoporous materials),  $\text{Fe}_3\text{O}_4@m\text{SiO}_2\text{-NH}_2\text{-CMCD}$  (mesoporous materials). As shown in Curve a, the first weight loss peak appeared below 120 °C, which is corresponded to a weight loss of 2.6% owing to adsorbed water. Compared with  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (Curve a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-CMCD}$  (Curve b) is thermally less stable owing to the presence of grafted CM- $\beta$ -CD on the surfaces of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ . A segmented drop of 7.3% was observed in the temperature range 320–760 °C, this missing was ascribed to the thermal decomposition of cross-linking agents (EDC and

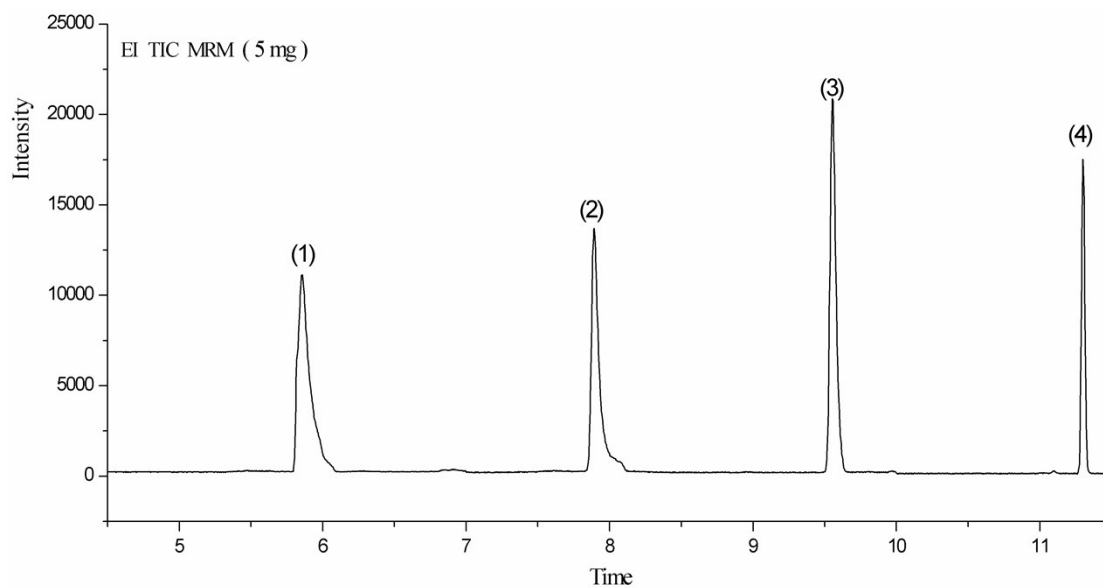
NHS) and CM- $\beta$ -CD. Compared with Curve b,  $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2\text{-CMCD}$  (Curve c) shows an obvious drop of 22.1% in the temperature range 320–760 °C. This means mesoporous  $\text{Fe}_3\text{O}_4@\text{mSiO}_2$  may carry more  $\beta$ -CD groups which may greatly improve the clean-up efficiency. In addition, the TGA curves have also confirmed that successful grafting of CM- $\beta$ -CD can be done on the surface of  $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2$ .

### Clean-up mechanism:

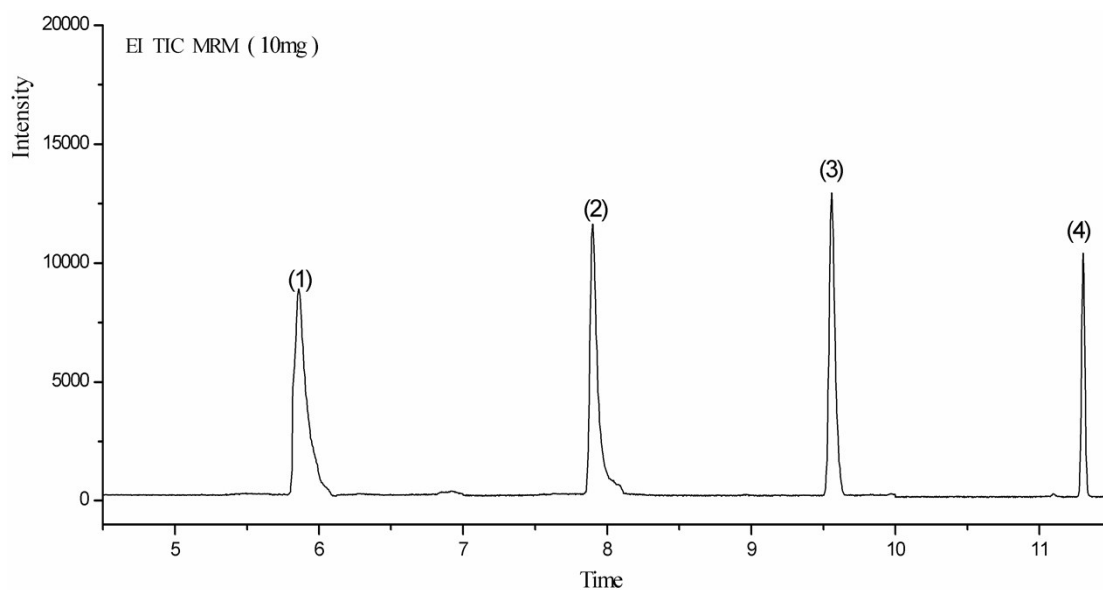
We design a series of experiment to verify the adsorption mechanism by using different amount of the  $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2\text{-CMCD}$  to adsorb various chlorobenzene. 100 ng of 1,3-Dichlorobenzene, 100 ng of 1,3,5-Trichlorobenzene, 100 ng of 1,2,3-Trichlorobenzene and 100 ng of 1,2,3,5-Tetrachlorobenzene were dissolved in 5 mL of acetonitrile. The tubes were vortex mixed for 10 min, then the mixed solution was centrifuged for 5 min. The supernatant was filtered through a polyamide syringe filter (25 mm, 0.22  $\mu\text{m}$ ) and concentrated. Finally, the residues were redissolved with 1 mL of isooctane in a volumetric flask for the GC-MS system.



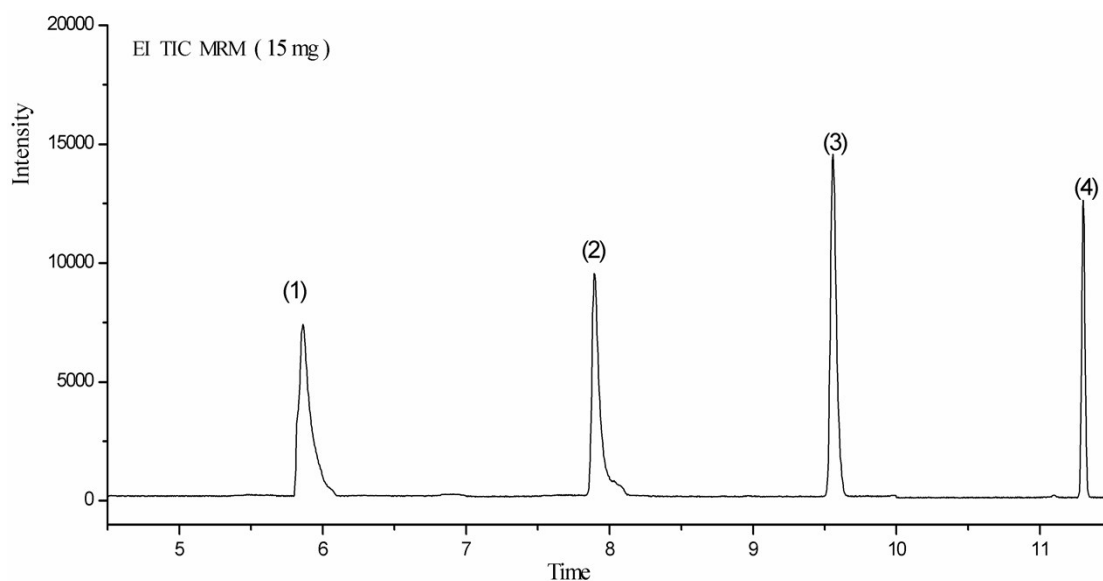
**Fig. S5** The GC-MS chromatogram of 0 mg of the  $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2\text{-CMCD}$  to adsorb various chlorobenzene with peak numbering: (1) 1,3-Dichlorobenzene; (2) 1,3,5-Trichlorobenzene; (3) 1,2,3-Trichlorobenzene; (4) 1,2,3,5-Tetrachlorobenzene



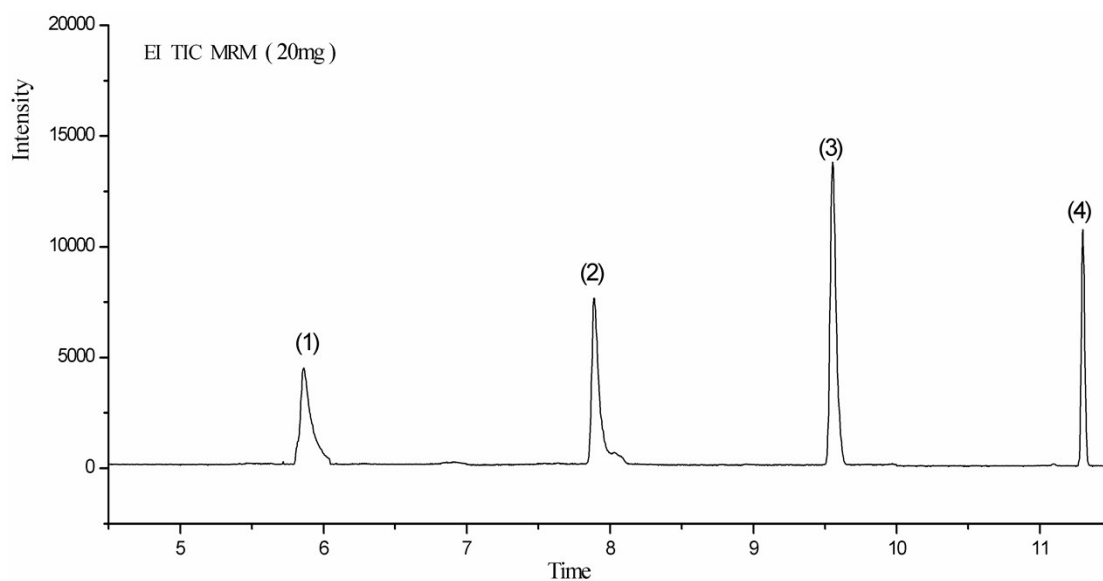
**Fig. S6** The GC-MS chromatogram of 5 mg of the Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD to absorb various chlorobenzene with peak numbering: (1) 1,3-Dichlorobenzene; (2) 1,3,5-Trichlorobenzene; (3) 1,2,3-Trichlorobenzene; (4) 1,2,3,5-Tetrachlorobenzene



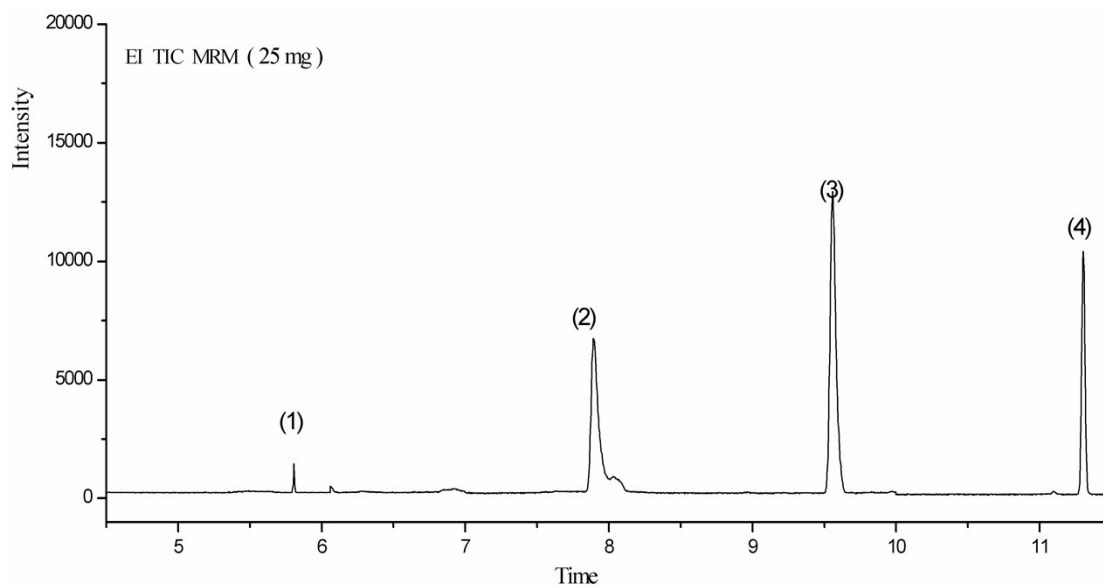
**Fig. S7** The GC-MS chromatogram of 10 mg of the Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD to absorb various chlorobenzene with peak numbering: (1) 1,3-Dichlorobenzene; (2) 1,3,5-Trichlorobenzene; (3) 1,2,3-Trichlorobenzene; (4) 1,2,3,5-Tetrachlorobenzene



**Fig. S8** The GC-MS chromatogram of 15 mg of the  $\text{Fe}_3\text{O}_4@m\text{SiO}_2\text{-NH}_2\text{-CMCD}$  to absorb various chlorobenzene with peak numbering: (1) 1,3-Dichlorobenzene; (2) 1,3,5-Trichlorobenzene; (3) 1,2,3-Trichlorobenzene; (4) 1,2,3,5-Tetrachlorobenzene



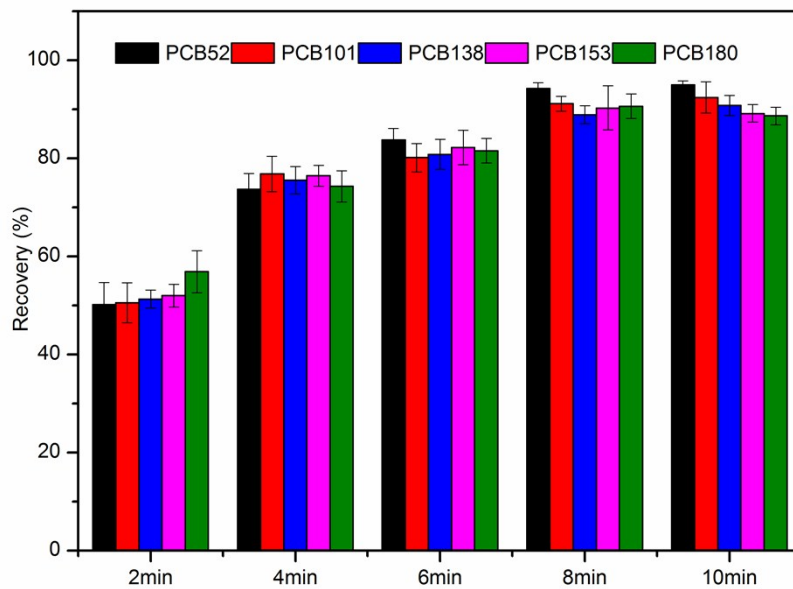
**Fig. S9** The GC-MS chromatogram of 20 mg of the  $\text{Fe}_3\text{O}_4@m\text{SiO}_2\text{-NH}_2\text{-CMCD}$  to absorb various chlorobenzene with peak numbering: (1) 1,3-Dichlorobenzene; (2) 1,3,5-Trichlorobenzene; (3) 1,2,3-Trichlorobenzene; (4) 1,2,3,5-Tetrachlorobenzene



**Fig. S10** The GC-MS chromatogram of 30 mg of the  $\text{Fe}_3\text{O}_4@m\text{SiO}_2\text{-NH}_2\text{-CMCD}$  to absorb various chlorobenzene with peak numbering: (1) 1,3-Dichlorobenzene; (2) 1,3,5-Trichlorobenzene; (3) 1,2,3-Trichlorobenzene; (4) 1,2,3,5-Tetrachlorobenzene

The results indicate that the chromatographic peaks of DDT, DDE, and DDD obviously reduced in acetonitrile. However, the peaks of highly chlorinated PCBs have almost no reduce, indicating that they are difficult to incorporate within the cavity of the  $\beta\text{-CD}$ . This could be attributed to the fact that the chlorinated benzene size of highly chlorinated PCBs may be too large to be accommodated by the  $\beta\text{-CD}$  cavity.

## The effect of dSPE time on the clean-up procedure

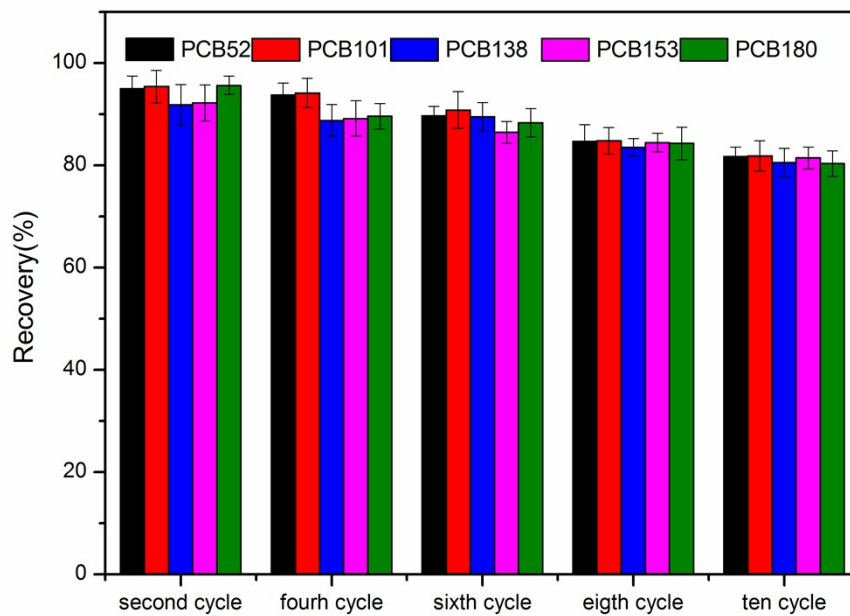


**Fig. S11** Recovery effect of five kinds of highly chlorinated PCBs on dSPE time

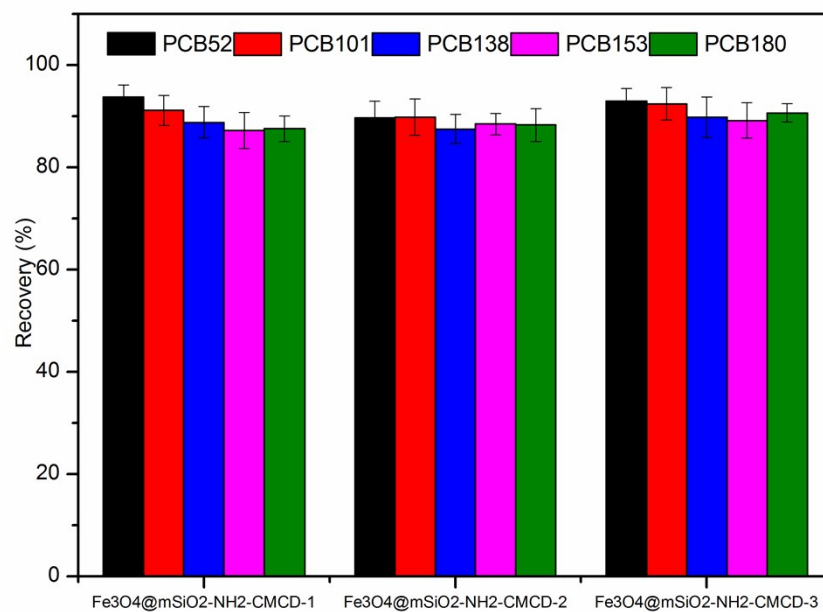


### **Recycling and reproducibility of Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD**

To investigate the recyclability and reproducibility of Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD, we used seafood samples spiked with five kinds of highly chlorinated PCBs at a concentration of 0.5 ng·g<sup>-1</sup> and 10.0 ng·g<sup>-1</sup>. In this experiment, we collected all adsorbent that were used for the dSPE clean-up procedure. Thereafter, we immersed these adsorbents in 0.1 mol·L<sup>-1</sup> NaOH solution for at least half an hour. Ultrasound-assisted solvent extraction was conducted on these adsorbents using DCM for 5 min. Then, they were washed with water to remove the redundant sodium hydroxide and DCM. These particles were finally dried under a vacuum at 60 °C for 6 h. The results of this recycling experiment indicated that the recoveries of at least 82.2% of all the remaining analytes were achieved by reusing Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD for ten times without sacrificing the clean-up efficiency (Fig. S12). Furthermore, we also evaluated the reproducibility of the Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD used for the dSPE clean-up procedure. Fig. S13 displays the recoveries of five kinds of highly chlorinated PCBs by the three batches of the adsorbents. The results indicate that the absolute deviation in the recoveries of each highly chlorinated PCB from the three batches is less than 5.0%, thereby indicating that the preparation of the adsorbent has satisfactory repeatability and reproducibility.



**Fig. S12** Recoveries of five kinds of highly chlorinated PCBs with the clean-up procedure via dSPE by reusing  $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2\text{-CMCD}$



**Fig. S13** Recoveries of five kinds of highly chlorinated PCBs on the clean-up procedure with three batches of  $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2\text{-CMCD}$

### **Synthesis of Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD**

The magnetic Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub> nanoparticles were synthesized as described in previous work [1]. Magnetite nanoparticles Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub> (0.5 g) were added to a freshly prepared solution of APTES (2% v/v) in water and the final volume was adjusted to 50 mL. The mixture was allowed to react with vigorous stirring for 8 h at 70 °C to obtain Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub> [2, 3]. The carboxymethyl-β-cyclodextrin modified Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub> nanospheres (Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD) were prepared using this stepwise process. First, 1 g of carboxymethyl-β-cyclodextrin was activated using 0.5 g of N-hydroxy succinimide and 0.5 g of N-(3-Dimethylaminopropyl)-N'-ethyl carbodiimide hydrochloride in phosphate buffer solution (100 mL, pH = 7.4) [4]. After conducting this reaction for 8 h at room temperature, the amino-functionalized magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>) were added and stirred for another 6 h to obtain the resulting adsorbents.

### **GC-MS analysis**

The GC-MS column used was RXi-5MS. The oven temperature program was 110 °C, held for 3 min, ramped 20 °C min<sup>-1</sup> to 230 °C, being held for 2 min, ramped 5 °C min<sup>-1</sup> to 245 °C, held for 1 min, then ramped 20 °C min<sup>-1</sup> to a final temperature of 280 °C, held for 1 min. Helium (purity 99,999%) was used as a carrier gas at a flow rate of 0.97 mL·min<sup>-1</sup>. Injections into the GC-MS were made using a 10.0 μL Hamilton syringe (Reno, NV, USA). The qualitative ion, quantitative ion, retention time of PCBs, DDT, DDE, and DDD was put in Table S1.

## **Comparison of different clean-up procedures**

### **Clean-up via C18 SPE column**

After extraction, the extract was subjected to clean-up with C18 column (C18 column was conditioned with 10 mL of methanol : water mixture (1:5, v/v), after loading, the sample was eluted with 20 mL of methanol and 20 mL of n-hexane:DCM (1:1, v/v) mixture at the flow rate of 1 mL·min<sup>-1</sup>. Subsequently, the extract was concentrated to ~ 1 mL and then dried by a gentle stream of nitrogen. Finally, the residues were redissolved with 1 mL of isooctane in a volumetric flask and filtered through a 0.22 µm membrane prior to its injection into the GC-MS system.

### **Clean-up via d-SPE with amino (-NH<sub>2</sub>) modified silica**

After extraction, the extract was concentrated to about 2 mL with acetonitrile. Acetonitrile solution addition was carried out in order to eliminate the loss of target analytes and guarantee it can be enriched in a weak-polar solvent before clean-up procedure. Subsequently, the adsorbents (50mg) were added in above solution, vortexed for 8 min. After 2 minutes standing, the supernatant was isolated by an external magnetic field and concentrated with a nitrogen stream. Finally, the residues were redissolved with 1 mL of isooctane in a volumetric flask and filtered through a 0.22 µm membrane prior to injection into the GC-MS.

### **Clean-up via d-SPE with Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD**

On the final extraction step, the dry residues were redissolved in 2 mL of acetonitrile. Subsequently, the 50 mg of Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub>-NH<sub>2</sub>-CMCD was added in

above solution, vortexed for 8 min. After 2 minutes on standing, the supernatant was isolated by magnet and concentrated with nitrogen stream. The residues were redissolved in 1 mL isooctane, vortexed, and transferred into a volumetric flask vial for GC-MS analysis.

### **Method validation**

Standard solution were prepared by dilution in isooctane and stored at 4 °C in the dark. Two kinds of working standard mixture solution (five kinds of highly chlorinated PCBs, three kinds of organochlorine (DDT, DDE, and DDD) and five kinds of highly chlorinated PCBs) was prepared by appropriate dilution of the stock solutions with isooctane. Spiked recoveries and matrix effects were performed at concentrations of 10 ng·g<sup>-1</sup> for clean-up procedures, 0.5 ng·g<sup>-1</sup> and 10 ng·g<sup>-1</sup> for method precision and accuracy. The spiked samples were homogenised in a mortar and stored at 4 °C for about 12 h. Recoveries at each level were run along with both reagent and a sample blank. The method was evaluated by linearity, LOD and LOQ, precision and accuracy. Matrix-matched calibration standards for fish and shellfish sample were spiked with concentration at 0.1, 2.5, 5.0, 10.0, 25.0, 50.0, 200.0 µg·L<sup>-1</sup> were prepared for the calibration curves. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated in blank extracts: these parameters were the lowest analyte concentrations that yielded a signal-to-noise (S/N) ratio of 3 and 10, respectively. Both the method precision and accuracy were estimated. The intra-day and inter-day precision were investigated by injection of the two levels of spiked samples (0.5 and 10.0 ng·g<sup>-1</sup>) with six replicates and replicated on six different days,

respectively. Accuracy of the method was also checked by spiking 0.5 and 10.0 ng·g<sup>-1</sup> of five kinds of highly chlorinated PCBs in the real samples.

## Reference

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